

A CONTRIBUTION
TO THE KNOWLEDGE OF
TELLURIUM

A DISSERTATION

Presented to the Board of University Studies of the Johns Hopkins

University for the Degree of Doctor of Philosophy

—BY—

FREDERICK HENRY DURYEA CRANE

1898

EASTON, PA.:
THE CHEMICAL PUBLISHING CO.
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A CONTRIBUTION TO THE KNOWLEDGE OF TELLURIUM.

In spite of its one hundred years of existence as a known substance, the nature of tellurium is almost as obscure as in the time of Berzelius. This has been largely due to its scarcity. It could only be gotten in small quantity by lengthy processes of extraction applied to large masses of crude ores. And, when obtained, it was still uncertain that it was the same substance that had before been described as derived from other sources, since the methods of purification were various, and imperfect. Moreover, the results of determinations of its atomic weight were conflicting.

The rise of the electric refining industry has placed within reach the dross which is produced in large quantities in the final purification of the precious metals, and it is with tellurium from this source that the following work has been conducted.

The Raw Material.

Large quantities of low grade gold and silver ores found in our Western States are now profitably worked by smelting them with copper ores, the matte thus obtained being again smelted, rolled into plates, and the copper electrically refined.

In the tanks in which this is done, the precious metals and the impurities collect as a black slime.¹

This is smelted with sand and niter and the silver and gold reduced and recovered. The slag is lixiviated, and the solution acidified with sulphuric acid. The voluminous white precipitate is allowed to settle; the acid liquid is then filtered off, and the mud dried at a low heat. A chalky, friable mass, with some harder portions due to greater heat in drying, results. It contains much silica, tellurium mostly as tellurite, with a little tellurate due to the drying, and some selenium,

¹ C. Whitehead: J. Am. Chem. Soc., 17, 849.

antimony, arsenic, copper, and other metals. There are varying amounts of iron and aluminium from the flux. Potassium is present in large quantity, but not sodium.

Extraction of Tellurium.

From this white substance the tellurium is readily extracted by repeated leaching of the powdered material with strong commercial hydrochloric acid. Heating the acid does not appear to be of much advantage. The best results are obtained when large quantities of it are used.

In order to filter the slimy mud at all rapidly, a good pump and as large a filtering surface as possible should be used. To make such a surface a 3.5 cm. Witte plate is put in a large funnel and covered with a rather thick layer of glass beads. On this is placed a layer of asbestos in the usual manner. This device allows lateral passage of the filtrate, and gives a much larger effective surface than the combined area of the holes of a plate alone.

The bright yellow hydrochloric acid solution which is obtained is evaporated to a convenient consistency, depending on its intended use. It contains considerable quantities of the metals which occur as impurities as well as the tellurium and selenium.

Precipitation of Tellurium.

Since the work of Berzelius the use of sulphur dioxide as a precipitant of tellurium has ordinarily been advised, although it has been known equally long that the action was never quite complete and that traces of other metals, as well as all the selenium, came down also. Its exceeding convenience however was a strong reason for its use in the present instance for at least the preliminary precipitation. It was found that, in all probability, the main reason for the incompleteness of its action was the very rapid increase in the ratio of acid to unprecipitated tellurium in the solution, two thirds of this being due to the hydrochloric acid set free, and one third to the sulphuric acid formed.

If these could be removed the precipitation should go on.

¹ Keller: J. Am. Chem. Soc., 19, 778.

Evaporation sufficed for the hydrochloric acid, and an additional quantity of tellurium was obtained, but the increase of the sulphuric acid soon stopped the reaction.

The practical removal of the acids by neutralization was then tried, and it was found that the addition of an alkali or alkali carbonate resulted in a renewed precipitation. At this point Mr. R. L. Whitehead advised the use of acid sodium (or potassium) sulphite; and his suggestion was thenceforward followed.

But even with this very efficient reagent the action in the cold is never quite complete. It was found that if a solution in which neither more acid sulphite, or more hydrochloric acid added to decompose some of the excess of acid sulphite already present, will produce a further precipitate, be heated to boiling, that there is then a further precipitation without any addition of reagents.

It is better to remove the first precipitate before boiling, as the action is then more evident. This new precipitate gives the qualitative reactions for tellurium, and differs from the first precipitate only slightly in tint. Its formation is probably due to the decomposition of some alkali tellurate at first formed through mass action. By this means, then, the tellurium was obtained, mixed with selenium and a little of the other impurities.

Precipitation of Tellurium by Magnesium.

In devising a method for the more accurate estimation of tellurium it was found that metallic magnesium would completely precipitate tellurium from a solution of the tetrachloride in hydrochloric acid. The excess of hydrochloric should be as small as possible, and a slight excess of magnesium should be added. This latter may be destroyed by vigorous boiling, when it decomposes the water; the magnesium hydroxide is then removed by acidifying very slightly with acetic acid. The well-washed tellurium precipitated by this method seems to be less easily oxidized.

Detection of Tellurium.

The apparent completeness of the action of acid sodium

sulphite led to the idea that it would detect small quantities of tellurium and do this more rapidly and efficiently than former methods. To test this, a weighed portion (0.107 gm.) of tellurium was dissolved in hydrochloric acid by the aid of as little chlorine gas as possible, and the solution gently heated to expel any excess of chlorine. It was then diluted with a little hydrochloric acid and then with water to 500 cc. Ten cc. of this solution gave a marked precipitate, so 10 cc. were diluted to 110 cc., and as the same quantity of this also gave a strong reaction, the dilution was repeated in a similar manner. An effective surface of about one half a square centimeter of white filter-paper was used to collect the precipitate, and on this the layer of black tellurium was plainly visible; the amount present per cc. of solution being 0.00000214 gram, and the total quantity used being 0.0000214 gram.

And the presence of tellurium was still discernable when the dilute solution contained only 0.000000214 gram per cc. and there was present but 0.00000214 gram.

It appears probable that this limit is due simply to the fact that we have here nearly reached the physiological limit of seeing black on white.

Detection of Selenium.

Mr. Edward Keller has recently called attention to the precipitation of selenium by ferrous sulphate,¹ and this reaction was tested in like manner, 0.1139 gram of selenium being weighed out, dissolved, and diluted. The precipitated selenium colored the paper with the bright, characteristic red when the dilution was 0.00000207 gram per cc., ten times that quantity being used. And at a dilution of 0.000000207 gram per cc. the precipitate from ten cc. was more easily seen than that of tellurium at about that dilution.

Furthermore, the precipitation of selenium at a dilution of 0.00000207 gram per cc. is independent of a little more than one hundred times as much tellurium as tetrachloride.

Precipitation of Tellurium by Ferrous Sulphate.

Mr. Keller² states that ferrous sulphate does not precipitate

¹ J. Am. Chem. Soc., 19, 771.

² Keller: *loc. cit.*

tellurium. The statement is evidently made with respect to a solution of the tetrachloride in hydrochloric acid, and if there is certainly only the tetrachloride present, it is quite true.

Ferrous sulphate, however, precipitates tellurium from a solution of the tetrachloride in hydrochloric acid if it has been boiled vigorously for some time, the evaporating acid being replenished; or if it is boiled, heated, or remains for some time in contact, with tellurium.

This seems to be due to the presence of tellurium dichloride. But tellurium dichloride, according to Rose,¹ breaks down in the presence of acids into tellurous acid and tellurium. To test this the two chlorides of tellurium were made, first by the direct action of chlorine on tellurium, and then by the action of this tetrachloride on the proper amount of tellurium. The solution which was obtained by treating the dichloride in the cold with hydrochloric acid gave a black precipitate with ferrous sulphate to a slight extent, and a solution made with the hot acid gave it much more markedly.

A mixture of the two chlorides treated with the acid gave a very decided precipitate, and a solution of the dichloride in a strong solution of the tetrachloride in hydrochloric acid, gave it most strongly of all. In all these experiments the known decomposition of the dichloride into free tellurium was prominent and evidently nearly in theoretical quantity, so all the solutions were well filtered before the ferrous sulphate was added.

The actual mass of the precipitated tellurium is small in comparison with the quantity present as chloride, but the deep black color and the very fine state of division make the appearance a marked one. The black precipitate collects and settles after a time, and seems to diminish in bulk.

This is no doubt the same sort of change as that which occurs in tellurium precipitated by sulphurous acid or acid sulphite, and that is likely akin to the changes in precipitated selenium and tellurium when heated.

Furthermore, a boiling solution of tetrachloride in hydrochloric acid will dissolve a little tellurium. In order to have

¹ Rose: *Pogg. Ann.*, **21**, 443.

the action complete, there must be but little of it, and that in a state of fine division.

This action may account in part for the apparent diminution of the precipitate just mentioned.

It is hard to keep a concentrated solution of the chloride in a condition in which it gives no precipitate with ferrous sulphate, but it may be quickly brought to such a condition by passing through it a few bubbles of chlorine, the excess of which is soon lost by allowing the solution to stand open a short time.

Purification of Tellurium.

The purification of tellurium in quantity appeared to be a question of getting rid of selenium on the one hand, and of various more metallic elements on the other. And it seemed advisable to do this as simply as possible in view of the uncertainty as to the individuality of the substance.

Suspicion has been cast, at various times, on all methods which require repeated evaporations, distillations, or crystallizations, or in which nitric acid must be removed by prolonged heating. Further, it has been directly alleged that distillation in hydrogen gave a product with a lower relative weight¹.

The method of Keler works well for selenium, if precaution is taken to prevent a reversal of the action through the mass action of the tellurium tetrachloride on the precipitated selenium, which will be referred to below.

But it has the great disadvantage of burdening the solution with iron salts and sulphuric acid, which latter always makes the precipitation of tellurium more difficult.

The method of Stolba² which depends on the reduction of a tellurate in alkaline solution by boiling with glucose, which reduction is claimed to begin and be completed before a similar action with any selenite present, appears to work as described. But in the presence of the excess of glucose and its decomposition products it is very hard to determine the limits of the reactions. Pure tellurium is unquestionably gotten at first, but the uniformity of the reaction remained in doubt. This process could doubtless be made to work well, but it was not used since that to be described seemed simpler.

¹ Brauner: J. Chem. Soc., 55, 392.

² Stolba: Jahresbericht 1873, 214.

As only a small fraction of the more metallic elements was carried down by the tellurium, it seemed probable that several precipitations would remove practically all of these. Consequently it was required to repeatedly convert the precipitated tellurium into the tetrachloride.

The direct action of gaseous chlorine on dry tellurium is very rapid, but much heat is evolved, enough, in fact, to volatilize a part of the chloride unless the process is carried on quite slowly. The action of gaseous chlorine on tellurium suspended in strong hydrochloric acid is, on the other hand, quite slow; and rapidly becomes slower as the quantity of dissolved chloride increases, and is very slow if the tellurium is at all compact.

It has long been known that tellurium is much more metallic than selenium, and that selenium is the first to be precipitated by sulphur dioxide. In fact this method has been suggested for their separation. Now it seemed probable that if the mixed precipitate could be subjected to the action of nascent chlorine, by being made the positive pole of an electrolytic cell containing hydrochloric acid, that not only would the tellurium be rapidly converted into the chloride, at a low temperature, but that also the more metallic tellurium would be first attacked, to the practical if not total exclusion of the selenium.

Preliminary trials on a small scale having shown the rapid action of the nascent chlorine, a larger apparatus was made. This consisted of a 750 cc. funnel with the stem ground square off. In the bottom of the funnel portion was placed a button of commutator carbon about 2.5 cm. in diameter, to which was soldered a small brass nut.

The button was sloped to fit the funnel and jacketed with a doubled rubber tube. Through the stem of the funnel was passed a heavy copper wire, threaded at both ends, and having on the lower end a small nut. The upper end of this wire was screwed into the nut on the button, and the button then drawn down tight by the lower nut acting against the lower end of the funnel stem. This formed the positive pole, the current being taken in on the wire.

The negative pole was formed of a sheet of thin copper of some 30 sq. cm., which was soldered to a convenient wire. This pole was never in the acid but a moment before the current was on, and was removed at once when it was off, so that it was not attacked by the acid. To prevent the deposition of tellurium it was inclosed in a little porous cell which was hung on the edge of the funnel. A small automatic drip supplied pure hydrochloric acid just fast enough to keep the surface of the liquid in the cell about 0.5 cm. above that in the funnel, so that there was always a flow of pure acid through the cell away from the negative pole. It was expected that the sloping sides of the funnel would keep the unattacked tellurium always at the bottom, but as the specific gravity of the solution increased, the solid did not sink rapidly enough, so a glass rod, mechanically turned, was put in to act as a stirrer. When somewhat heated from the passage of the current, this arrangement had a very constant resistance of a little more than half an ohm, and, with the current employed, used about nine amperes.

Practically, every trace of the chlorine liberated was absorbed, and consequently the speed of solution depended directly on the current. The first charge of the cell was not quite all dissolved when it became necessary to stop the action over night, and the entire contents of the cell were removed to another vessel. At the same time a portion of the liquid was taken out and tested for selenium, which was found to be present. Evidently the tellurium was not exclusively or primarily attacked, as some of it visibly remained. The next morning this test was repeated, and no selenium was found. And the reddish color of the sediment indicated that it had been precipitated. This electrolytic chlorine method of solution is very efficient and has the marked advantage of adding no extraneous substance. It is more rapid, of course, as the tellurium is the more finely divided.

Separation of Selenium by Tellurium.

Further experiments showed that if to a mixture of selenium dichloride, and tellurium tetrachloride dissolved in

hydrochloric acid tellurium be added, or a portion of the tellurium precipitated, and the mixture allowed to stand for some time, or better, and much more expeditiously, boiled, all the selenium will disappear from the solution, and may be found in the sediment, with the excess of tellurium. If the action takes place at the ordinary room temperature, the selenium can easily be seen on account of its color, but if heat is used the well-known change to the black form will occur, and it cannot be distinguished from the tellurium.

It may be readily detected, however, by filtering off the black residue and dissolving it in a little hydrochloric acid by the aid of chlorine, when the selenium may be again precipitated. If this reaction be carried on upon a microscope slide, it can be well seen and makes a rather pretty effect when magnified to about 80 diameters.

On a large scale it is preferable to heat the solution of mixed chlorides gently just below the boiling-point, and to have the tellurium in as fine state of division as possible and well mixed with the fluid. To attain both these ends it is advisable to precipitate some of the tellurium, either by leading in a little sulphur dioxide, or adding a little acid sulphite. The turbid liquid which results does not clear for some time by settling.

That this process is complete is shown by the fact that it not only removed selenium from tellurium tetrachloride solutions so completely that none could be detected by the ferrous sulphate test, but also removed selenium completely from a solution of selenium dichloride in hydrochloric acid, previously precipitated tellurium being employed. In this experiment tellurium is found in solution which shows conclusively a replacement or an exchange.

If, on the other hand, selenium be gently heated in a solution of tellurium tetrachloride for some hours, the addition of ferrous sulphate to the filtered fluid will show that a very small part of the selenium has gone into solution. This minute amount may be entirely removed by the treatment with tellurium. This seems to explain the observation that in working with quite large quantities of the mixed chlorides

in solution, the action of ferrous sulphate even in obvious excess did not seem to be quite complete if a few hours elapsed before the precipitated selenium was filtered off. But the solution could not be made to take up selenium if there was a little tellurium present, and it was kept well stirred. The phenomenon appears to be, to some extent at least, one of mass action.

In using this process for the removal of selenium, the precipitate, containing the excess of tellurium, is filtered off and redissolved, either by nascent chlorine or by conducting into it, suspended in hydrochloric acid, a stream of that gas. The selenium is then easily removed by ferrous sulphate and the tellurium by acid sulphite. It is well to avoid the use of nitric acid.

The Further Purification of Tellurium.

The logical sequence to boiling the mixed chlorides with tellurium in order to precipitate selenium or any less metallic elements was to boil the precipitated tellurium with a reserved portion of that solution from which it had been obtained, so that any more metallic elements which might have been carried down would be dissolved, and precipitate an equivalent quantity of tellurium. This was done, although several precipitations in the ordinary manner seemed to have already removed those traces of metals which have been previously noted as occurring in the crude material.

The tellurium prepared in this manner has the usual appearance and reactions, and could be completely distilled in a current of hydrogen, leaving only a slight residue of carbonaceous material probably derived from the filter-papers. It was noted that there was very little tendency to form hydrogen telluride with pure, dry hydrogen.

This process should tend to separate the suspected homologue of tellurium of greater relative weight, and although no definite indications of such a substance have been met with up to the present, work will be continued along this line if time and opportunity are found.

Determination of Tellurium.

There has never been any sure method of determining tellurium. Most observers have either determined other elements in the tellurium compounds, or precipitated the tellurium, treated it with nitric acid, and converted the compound thus formed into the dioxide by heat. This has been the most exact method.

But Brauner¹ notes the brown decomposition which Staudenmaier² had observed, and further claims that the nitric acid is not wholly driven off before a part of the dioxide is volatilized. A method of avoiding the brown color has lately been given by Norris and Fay,³ but nothing is said as to the removal of the nitric acid, and there is visible volatilization. But gravimetric determinations by the method about to be described showed that the dioxide prepared by that method was quite pure. However, it is doubtful if nitric acid can be removed without some volatilization.

No volumetric method which does not require a correction term, with the exception of that of Norris and Fay, has been devised. The objections to the direct precipitation and weighing of the tellurium were alleged to be two; that it was not possible to precipitate all the tellurium from an acid solution, and that after precipitation it was oxidized so much in drying that the results were variable.⁴

In view of the extreme delicacy of the acid sodium sulphite when used to detect tellurium, it seemed advisable to try it as a precipitating agent in quantitative work.

There is no doubt that free acid does prevent the complete action of sulphur dioxide, but there is no evidence that neutral alkali salts in solution do this, if the solution is heated; at least qualitative experiments failed to show such an action.

So it is only needful to add enough acid sulphite to give up soda to the acids present and set free. A slight excess of sulphite does no harm, and an excess of sulphur dioxide is readily removed.

¹ Brauner : *Loc. cit.*

² Staudenmaier : *Ztschr. anorg. Chem.*, **10**, 206.

³ Norris and Fay : *Am. Chem. J.*, **20**, 278.

⁴ Brauner : *Loc. cit.* ; Norris and Fay : *Loc. cit.*

After the acid sulphite has been added, it is advisable to let the mixture stand for a time, usually, for convenience, over night, as the precipitate seems to be in better mechanical form when this is done. But the action may be completed at once by heating. At any rate, the liquid with the precipitate still in it should be raised to the boiling-point for a short time.

This is to gain two ends: to insure the total precipitation of the tellurium, which is never quite complete in the cold when large amounts are being handled (as has been noted); and to cause some definite but undetermined change in the precipitate. As a result of this it becomes much easier to filter and wash, and less liable to oxidation.

This change, as has been said, seems to be like the long known change in selenium. It is hard to describe, but easily recognized, although it consists only of the merest change in tint and a difference in the manner in which the precipitate settles.

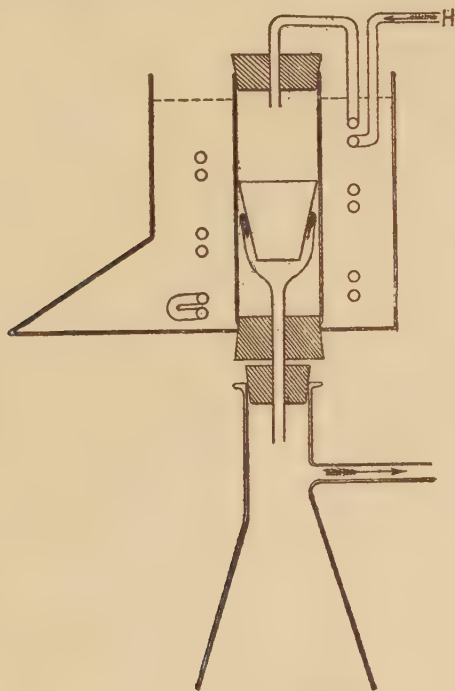
The precipitate is then collected on a Gooch filter and very thoroughly washed, care being taken that it is always covered with water. If speed is more requisite than exactness it may now be pumped as dry as possible, quickly dried in an air-bath, and weighed. It will oxidize to some extent, but by no means seriously.

The oxidation can easily be detected and the extent of it quite accurately judged by removing the precipitate with the filter surface, after weighing, and putting it in a beaker on a white surface, or in an evaporating dish and moistening it with a few drops of strong hydrochloric acid. A yellow tint of dissolved chloride appears at once only if oxidation has occurred, as unoxidized tellurium does not color hydrochloric acid. But if this preparation be allowed to stand, a color will appear, as the air acts readily on the acid mud. To determine how far this color could be used as a criterion of the presence of oxide and its amount, a weighed portion, 0.0068 gram, of pure tellurium tetrachloride was dissolved in strong hydrochloric acid and diluted. The yellow color of a layer 0.25 cm. thick was plainly visible when 0.00013 gram of tetrachloride was present in each cc.

To see if the method without special precautions in drying was even nearly correct, portions of a pure precipitated tellurium in which very little oxidation had occurred were weighed out, dissolved in a little hydrochloric acid by the aid of chlorine gas and treated as stated above.

Taken. Gram.	Found. Gram.	Gain. Gram.	Recovered. Per cent.
0.1768	0.1779	0.0011	100.6
0.1285	0.1289	0.0004	100.3

Probably practice in its use would make this method exact enough for all practical purposes. From the article by Mr. Keller already referred to, it appears that no special precautions in drying are used at the works of the Baltimore Electric Refining Company.



Device for Filtering.

To prevent, if possible, any oxidation, the filtering crucible was enclosed in a cylinder through which dry, pure hydrogen

which had just been passed over hot platinized asbestos was slowly drawn under slightly diminished pressure. The device was so arranged that it was not necessary to remove it from the filter flask, and a J-tube in the pump connection was joined to a mercury safety valve by which both the pressure and flow were regulated.

The cylinder and its contents were heated by jacketing them with a strong solution of calcium chloride, after the manner of a hot water funnel, and this bath was also used to warm the entering stream of hydrogen.

This arrangement prevents oxidation as far as can be detected by the coloration of hydrochloric acid, and as the results seem quite constant, it probably does not occur to a measurable extent. There is no evidence to show that tellurium which has been boiled with water can decompose water in the presence of hydrogen, so that the essential thing is to have pure hydrogen.

The Method.—The entire process is as follows: The given compound is so treated that the tellurium is in the form of the tetrachloride, avoiding, if possible, the use of nitric acid, and as little hydrochloric acid as possible being used. The solution is now diluted with water, but not to such an extent that a white substance appears, although a little of this seems to do no harm. The objection to a larger quantity is mechanical, the interior of the flocculent masses seems sometimes to be unattacked by the sulphurous acid.

A solution of acid sodium or potassium sulphite is now added. It should be moderately concentrated, and the quantity should be such as to neutralize nearly exactly the acids present and set free by the base of the reagent.

The excess of sulphur dioxide will escape harmlessly, but anything more than a slight excess of the acid sulphite is detrimental. The mixture, which has turned dark, has been gently agitated during these manipulations; it is now diluted to about 50–75 cc. and allowed to stand for a time as the precipitate thus seems to form more evenly. But it may be warmed at once.

If too much sulphite has inadvertently been added the precipitate should be decanted and reserved, and the precipitate washed once or twice and the decanted wash-water added to the other, and all this passed through the weighed filter later. The reason for this is that it is very hard to decant without getting some of the precipitate over, although it may remain invisible until it blackens the filter. If time is not a consideration, this decantation process may well be employed in all cases.

The precipitate, in about 75 cc. of water, is now gently warmed, being stirred with a glass rod tipped with a bit of rubber tube, both to prevent "bumping" and to detach those portions which at times form a very marked "mirror" on the sides of the vessel; it is allowed to boil rapidly for a moment or two, and then set aside. A little water from a wash-bottle may be added, as it aids the settling. The tellurium, which has changed in appearance, should settle very quickly. If it does not, it may be boiled a little more, but it is to be noted that differences in the concentration of the solution in which the precipitation took place may markedly influence the character of the precipitate.

The amount of material taken should be such that the tellurium will form a rather thin layer in the filter even while still wet. The precipitate is now filtered through a weighed filter, care being taken to keep it always covered with water, and well washed, and since there is no reason to suspect any action of the water, the washing should be thorough.

After the washing is completed the hydrogen supply is connected at once, the last water being followed through the filter by the hydrogen. But no effort need be made to displace the small amount of air in the cylinder.

The temperature of the calcium-chloride bath is now quickly raised to about 110° and kept there till the tellurium is dry. This must be judged from its appearance.

The filter is then removed to a desiccator, and, when cool, weighed. There is no tendency to oxidize rapidly in the air if thoroughly dry. The main danger to be avoided is the ac-

cidental access of air to the wet tellurium.

Some of the results obtained by this method were as follows:

Tellurium dioxide from the nitrate, $\text{Te} = 127.6$; $\text{O} = 16$.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.1047	0.0838	79.95	80.03
0.1130	0.0904	79.95	80.00

Tellurium tetrachloride distilled in carbon dioxide, $\text{Cl} = 35.5$.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.3879	0.1857	47.33	47.87
0.5678	0.2717	47.33	47.85

Tellurium oxychloride, fused.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.62075	0.3689	59.46	59.43

Tellurous acid, from the chloride.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.11985	0.0862	71.84	71.92

A Yellow Form of the Dioxide.

If a solution of tellurium tetrachloride in hydrochloric acid which has stood for some time after the selenium has been precipitated by ferrous sulphate and removed, or a similar solution to which ferrous or ferric chloride has been added, is diluted with water, a white precipitate forms. If this is now allowed to stand for a time, the excess of water being decanted and replaced till it is not colored by the iron, a heavy yellow precipitate will appear. Or if the solution is poured directly into boiling water, the whole mass of precipitate will be colored yellow. The difference in specific gravity is so great that the remaining white substance may be almost completely removed by washing.

This substance is easily soluble in hydrochloric acid, and more difficultly in nitric and sulphuric acids.

It is readily and completely dissolved by alkalies to a colorless solution without residue. Under the microscope it is seen to consist of more or less regular yellow crystals, of the iso-

metric system, octahedrons, sometimes modified by cubic faces. Among these were traces of a white substance which seemed to cling to the crystals. It appears to be a form of tellurium dioxide, analyses giving the following percentages of tellurium: 79.46, 79.52, 79.51, 79.58, 79.46; calculated for TeO_2 , 79.95. The discrepancy may be due to the adherent white substance, or to a little iron, of which a trace may be found by the ferrocyanide and sulphocyanide tests. To this also may be due the yellow color, which is very persistent, not yielding to nitric acid till the substance is all in solution, but the solution is colorless and deposits white crystals.

Decomposition of the Tetrachloride.

If water is added to a portion of the distilled tetrachloride of tellurium considerable heat is evolved and it passes into solution as a yellow liquid. If more water be added there is a curdy white substance formed, which settles and after a time forms the crystalline dioxide. The white substance is tellurous acid, but the wash water from it constantly contains a trace of chlorine, and there may be a little of some sort of oxychloride present. But if there is also present another metal, as iron, and particularly if antimony or arsenic is present, there is a marked change in the character of the white substance. It remains unchanged in water for days, and may be washed, dried, and redissolved and reprecipitated several times without forming the dioxide; and no fixed amount of tellurium was found in various samples. It appears to be a double oxychloride, and will be the subject of further investigation if possible.

Failure to Form Analogues of Thiosulphate.

The attempt was made to form substances analogous to thiosulphates by boiling sodium tellurite with sulphur, selenium, and tellurium, but after several hours no trace of any action could be found.

Instability of the Chlorides.

Many minor observations as well as those already noted,

tend to show that the chlorides of tellurium tend to pass to a slight extent from one to the other. This is especially true of the tetrachloride, which darkens on distilling in dry carbon dioxide. It is to this that the high per cent. of tellurium noted above is probably due. And even that distilled in chlorine will give a slight cloud with ferrous sulphate if it has been kept for a time.

Conclusions.

Tellurium may be easily obtained from certain wastes of electric refineries by extracting with hydrochloric acid and precipitating with acid sodium sulphite. Magnesium will also precipitate tellurium, and has some advantages for qualitative work, and also for quantitative. Tellurium may be detected in very dilute solutions by acid sulphite, and ferrous sulphate is equally sensitive with selenium, and is independent of tellurium tetrachloride. But ferrous sulphate precipitates tellurium under some circumstances, which is probably because some tellurium dichloride is present in solution.

In order to avoid certain sources of suspected error, and to add nothing but hydrochloric acid as reagent, a method of dissolving tellurium by electrolytic chlorine was devised, and was found to work rapidly and well.

While using this it was found that tellurium would remove selenium. The use of tellurium for this purpose rather than any other reagent is of advantage because it does not add any other elements to the solution, or permit the escape of any portion of the tellurium beyond control. This replacement method may be extended to remove more metallic elements.

Tellurium may be determined by precipitating with magnesium or acid sodium sulphite, boiling, drying in hydrogen, and weighing as tellurium.

The decomposition of the tetrachloride by water is not a simple matter, and becomes much more complex if other metals are present. The pure tetrachloride gives tellurous acid which decomposes to tellurium dioxide.

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